

Torsional Braid as a Kinetic Tool for the Study of the Polymerization of Viscous Materials.

I. Initial Studies

ARNOLD ADICOFF, *Research Department*, and
ARNOLD A. YUKELSON, *Propulsion Development Department*,
U. S. Naval Ordnance Test Station, China Lake, California

Synopsis

The torsional braid experiment of Lewis and Gillham has been so modified that kinetic parameters can be obtained in polymerizations conducted with viscous prepolymers. The relative rigidity curve is interpreted in terms of extent of cure. The activation energy for the polymerization of a carboxyl-terminated polybutadiene with an aziridinyl compound has been measured.

INTRODUCTION

The torsional braid has been used as a qualitative tool in the investigation of polymeric materials.¹⁻⁵ The apparatus consists basically of a pendulum composed of a demountable crossarm which is weighted at both ends (Fig. 1). The pendulum is supported by a filament (braid) which is rigidly held from above. The application of a torque to the pendulum, displacing the pendulum from its rest position, results in a number of oscillations when the pendulum is allowed to swing freely. The oscillations are timed and the oscillation period is obtained.

In the past, the torsional pendulum has not been used as a kinetic tool because of the lack of reproducibility in the impregnation of the braid by a polymerizable substance. Also, the interpretation of the significance of the resulting curve with respect to the kinetic parameters has not been entirely satisfactory. These inadequacies have been overcome, permitting the use of the torsional braid as a tool for the study of polymerization kinetics.

EXPERIMENTAL

Supporting Braid Evaluation

The support materials used were J. C. Higgins 27 lb. test braided nylon surf line, Conso twisted cotton carpet thread, 4 oz. No. 18, and Newton's braided cotton fishing line (Newton Line Co., Homer, N. Y.) No. 8005



Fig. 1. Inertial mass of torsional pendulum.

Size 5 (0.030 in. diameter). The support material was selected by choosing the braid which showed the smallest rigidity change caused by creep and temperature changes.

Method of String Preparation

Removal of Sizing. The cotton carpet thread and the braided cotton fishing line were desized by boiling for 1 hr. in 1 liter of 2% Na_2CO_3 solution, rinsing in tap water, boiling another hour in distilled water, and finally rinsing with distilled water. The treated string was then dried overnight at 80°C . *in vacuo*.

String Impregnation. The string was impregnated with resin under vacuum. An uncoated end was left for handling purposes. The vacuum treatment assured that the resin described in the gel content measurements impregnated the string.

Uniform Coating of Braid. The resin on the braid was uniformly distributed on the braid by drawing the impregnated braid through a specially prepared split die with an 0.029-in. orifice (Fig. 2) at a uniform rate (15. in./min.) by using a gear reduced electric motor.

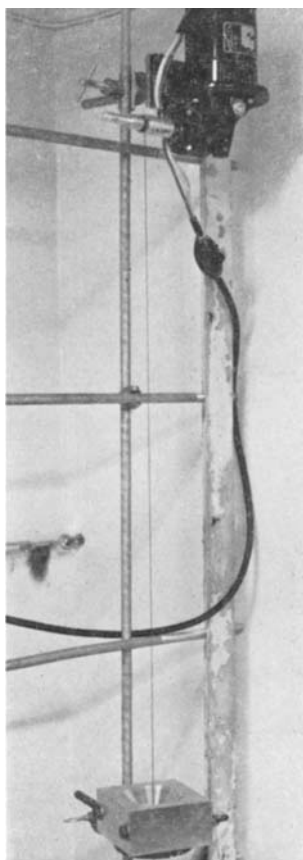


Fig. 2. Apparatus for depositing a uniform coating on braid.

Experimental Design and Instrumentation

The coated braids were cut to lengths of $16\frac{1}{2}$ –17 in. and clamped in two pin vises so that 16 – $16\frac{1}{2}$ in. of braid was between the chucks of the pin vises (Fig. 3). The lower pin vise is part of the weight support of the torsional pendulum while the upper pin vise has a hollowed section for admitting dry, preheated nitrogen gas. The clamped braid was lowered into the controlled atmosphere and temperature chamber (two chambers may be used simultaneously as illustrated in Fig. 4) and the demountable weighted pendulum crossarm attached.

With the apparatus sealed, the resin-impregnated braid was cured at a temperature controlled to $\pm 0.1^\circ\text{C}$. in an atmosphere of dry nitrogen. Periodically, the pendulums were torsionally displaced by means of electromagnets located between the two apparatus (Fig. 5). The reflection of a fixed light beam from a mirror mounted on the pendulum shaft (Fig. 1) activated a fixed photocell. The generated signal was amplified and a trace (Fig. 6) for counting and timing the oscillations was produced by a two-

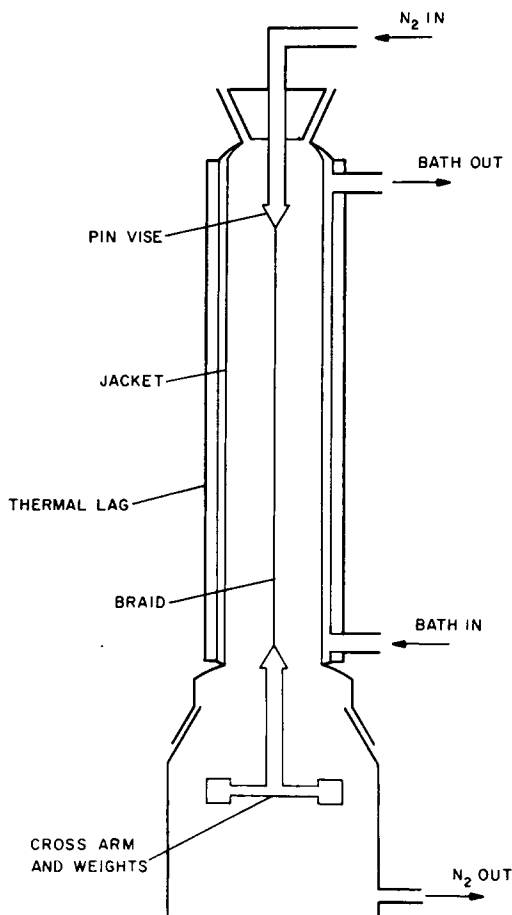


Fig. 3. Torsional braid apparatus (diagramatic).

channel direct-writing oscillograph, Model BL 202 (Brush Instruments, Division of Clevite Corp., Cleveland, Ohio).

Polymerization Experiments

Gel Content Measurements. Weighed quantities of a 1:1 equivalent ratio of a carboxyl-terminated polybutadiene (Butarez CTL type II, Phillips Petroleum Co., Bartlesville, Oklahoma) and tris[1-(2-methyl)-aziridinyl]phosphine oxide (MAPO) (Interchemical Corp., New York, N. Y.) were placed in reaction tubes and sealed under nitrogen. These were placed in a 70°C. bath and were withdrawn periodically, dissolved, and dispersed in a large excess of toluene and filtered. The residue was carefully washed with toluene and dried. From the dry weight, the gel content was determined.

Polymerization Rates. The braid coated with the above indicated formulation was polymerized at five temperatures; 50, 60, 70, 80, and 90°C.

The period of the pendulum was measured continuously at 30 min. intervals until the resin had achieved an advanced state of cure.

Calculations

The period of the torsional pendulum was used to calculate the relative rigidity of the resin-impregnated string. The relative rigidity, \bar{G}/\bar{G}_0 , is the ratio of the apparent rigidity modulus \bar{G} at a time t to the apparent rigidity

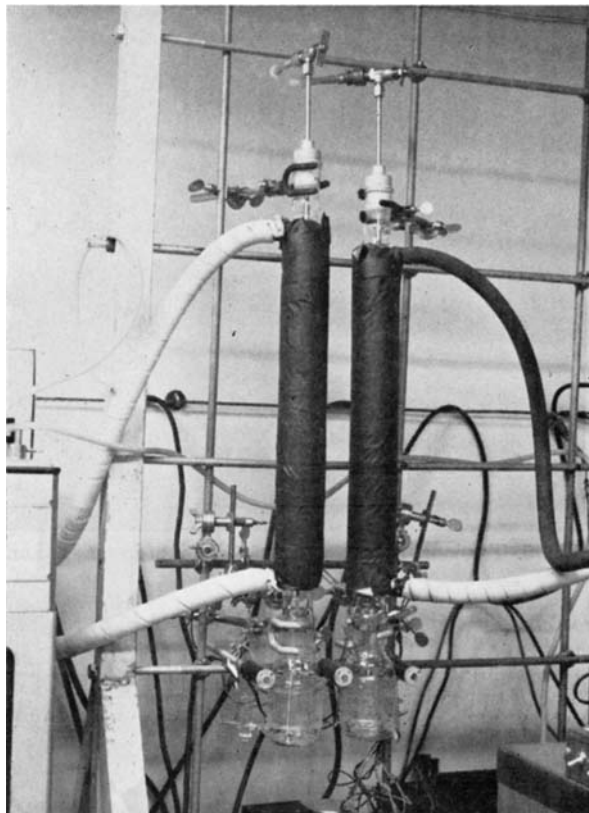


Fig. 4. Torsional braid apparatus.

modulus \bar{G}_0 at the start of the experiment.² The equation for the apparent rigidity modulus is derived from a modification of the equation for the rigidity modulus of a rod of uniform composition and dimensions. Thus,

$$\bar{G} = 8\pi L f_t^2 I / r^4$$

where L is rod length, f_t the resonance frequency of rod at time t , (f_0 the resonance frequency of rod at start of experiment,) I the moment of inertia, and r the radius of rod. The relative rigidity \bar{G}/\bar{G}_0 is proportional to f_t^2/f_0^2 .

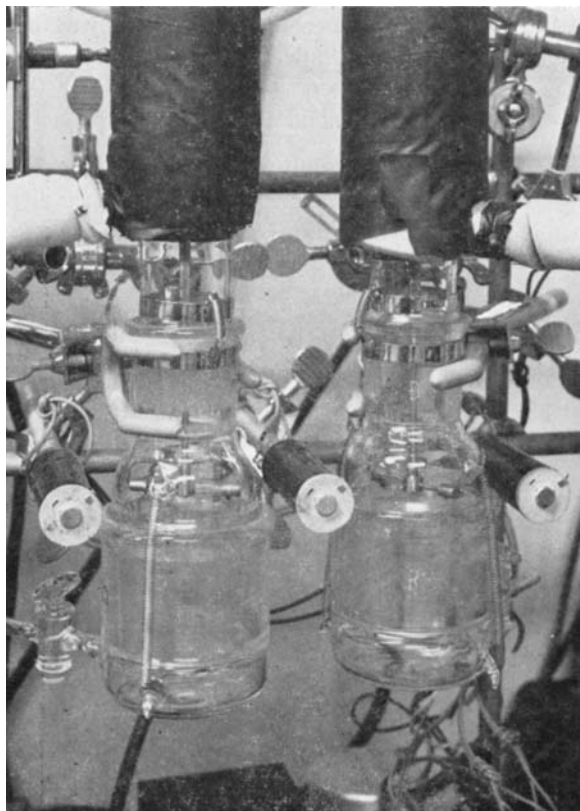


Fig. 5. Torsional braid apparatus: detail of lower section.

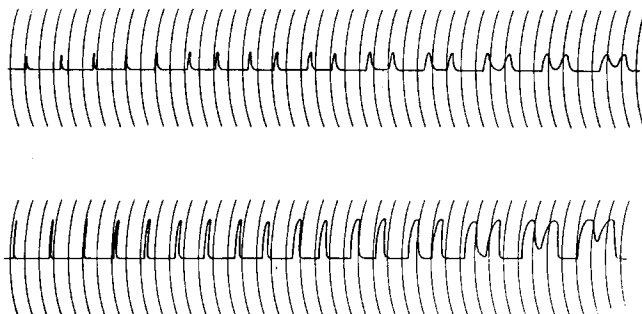


Fig. 6. Oscillograph trace of torsional oscillations of coated braid.

RESULTS AND DISCUSSION

Selection of Braid Substrate

Of the three braids used, only the cotton braided line appeared satisfactory. Contrary to the experience of Lewis and Gillham, the twisted cotton carpet thread appeared to be unsatisfactory in that when the

pendulum with the untreated thread was displaced, the oscillations were damped more rapidly in one direction than in the other. The nylon braid appeared to creep under the stress caused by the pendulum weight, giving a substrate with a changing cross section and changing period. This effect was enhanced as the temperature was changed. Some slight creep was experienced with the cotton braided fish line, but the modulus change caused by creep was very small compared to the total modulus change that occurred as the coated braid was polymerized.

Reproducibility of Resin Coating on Support Medium

The uniformity of the weight of the resin deposited under vacuum in the desized braided cotton fishing line is seen in the data in Table I. These samples of cotton line were impregnated with resin under vacuum and drawn through the split die at a uniform rate.

TABLE I
Reproducibility of Impregnated Cotton Braid

Sample	Weight of resin on a 15-in. section of braid, g.
1	0.0731
2	0.0711
3	0.0704
4	0.0714
5	0.0712
Average	0.0714
Mean	0.0712

Significance of Polymerization Curves

The polymerization curves are represented by plots of \bar{G}/\bar{G}_0 vs. time. They normally exhibit a line, before gelation occurs, of slowly increasing relative rigidity with time and a post-gelation line of greatly increasing relative rigidity with time (Fig. 7).

Correlation of Gel Formation with String Rigidity

The relative rigidity of a Butarez CTL type II-MAPO system at 70°C. was plotted as a function of gel content of the same system (Fig. 8). The coincidence of the sharp change in the shape of the curve strongly indicates that the gel point of the system is accompanied by a sharp change in the relative rigidity. Since the gel point is a function of the ratios of the functional group concentration assuming that neither of the components can react with itself,⁶ then one can consider that the gel point, for any fixed concentration condition, is invariant with respect to the extent of reaction required for gelation to occur. The time for gelation to occur is therefore a measure of the time for the system to achieve a fixed degree of conversion to polymer. The gel time is a measure of the polymerization rate.

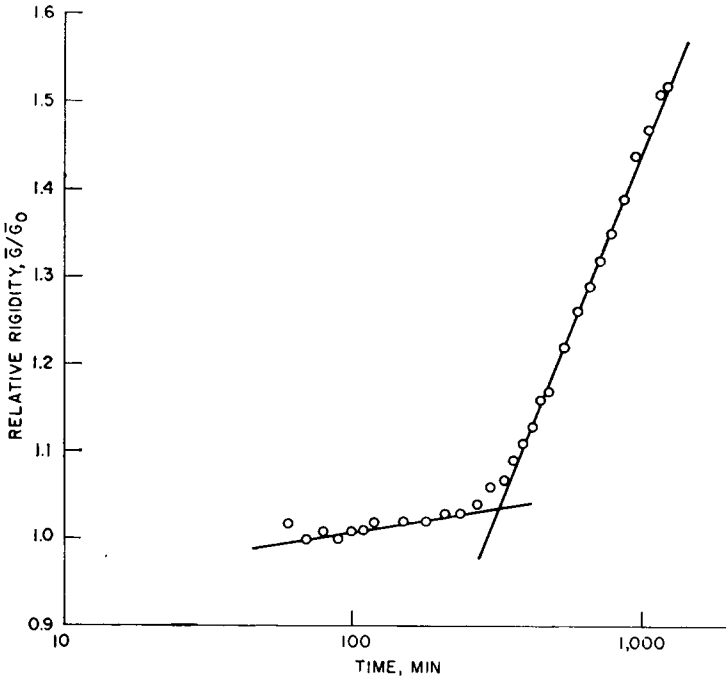


Fig. 7. Polymerization curve: gelation time at 70°C.; CTPB-MAPO System.

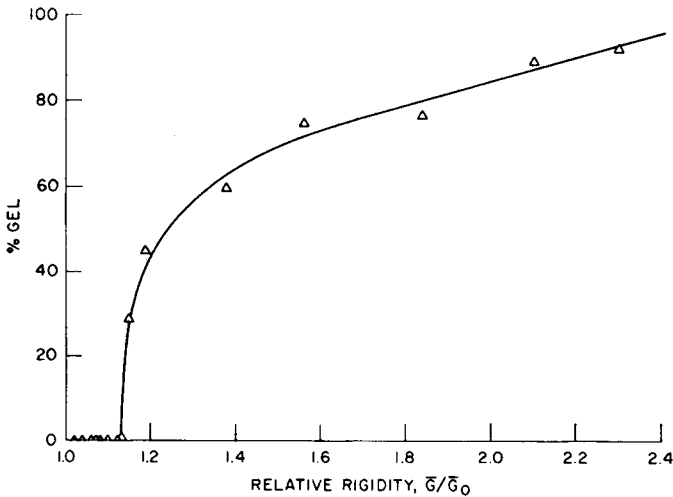


Fig. 8. Correlation of gel formation with resin-impregnated braid rigidity at 70°C., CTPB-MAPO System.

Torsional Braid Experiment

Analysis of the Data. It has been determined that with the present version of this pendulum a problem exists in that the modulus of an uncoated

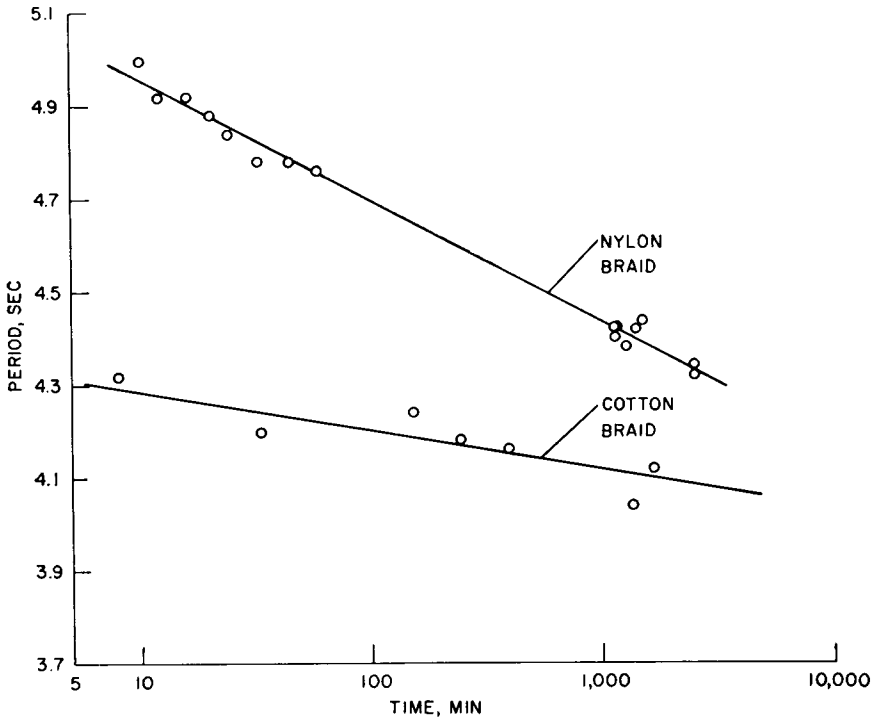


Fig. 9. Period change of supporting braid at constant stress (room temperature).

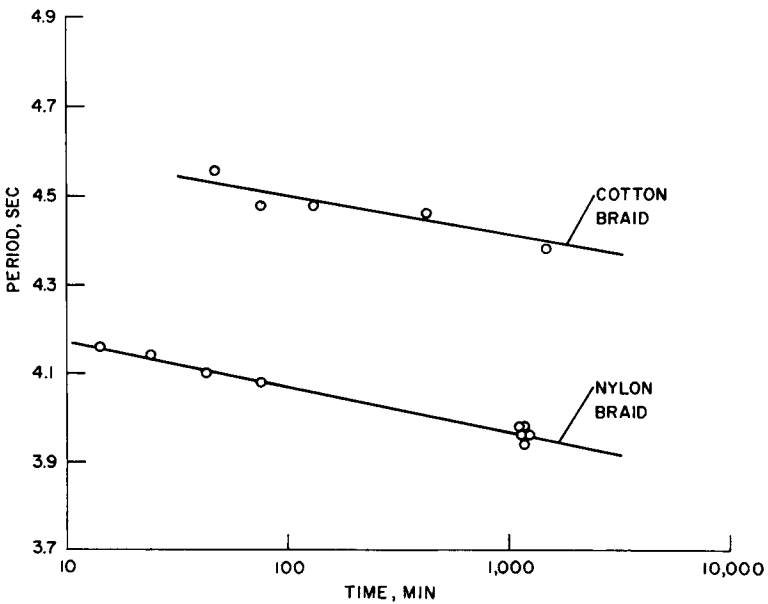


Fig. 10. Period change of supporting braid at constant stress (70°C).

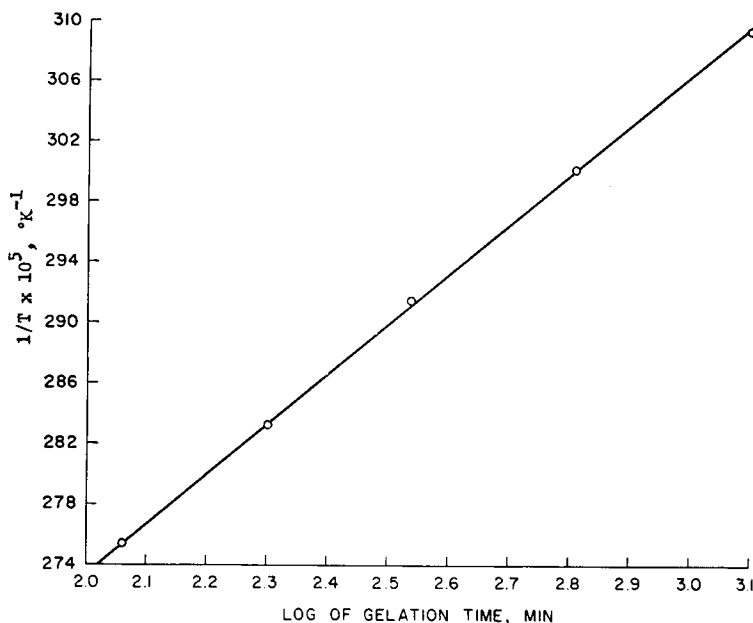


Fig. 11. Arrhenius plot for carboxy-terminated polybutadiene-MAPO reaction.

braid will change with time (Figs. 9 and 10) because of the creep manifested by the braid. When this change is small relative to the anticipated total change and when the relative rigidity is used rather than the modulus, errors caused by this effect are minimized. Nevertheless, one must choose the substrate carefully. It is possible to modify the pendulum further to remove this variable. For the purposes contemplated in these experiments this modification was not necessary. In the case that a nylon or polyethylene braid be required such a modification may prove to be essential.

Polymerization Results. The results of the polymerization of Butarez II with MAPO at a 1:1 equivalent ratio at various temperatures given are in Table II. The Arrhenius plot of this data is seen in Figure 11. From this plot an activation energy of 13.8 kcal./mole has been calculated for this polymerization reaction.

TABLE II
CTPB (Butarez CTL Type II) and MAPO, 1:1 Functional Ratio

Temperature, °C.	Time to gelation, min.
90	115
80	200
70	344
60	645
50	1250

CONCLUSION

The torsional braid of Lewis and Gillham has been modified and a technique for kinetic measurement developed. When used with viscous polymers, the instrument can be a kinetic tool for exploring the polymerization of crosslinking systems to and through gel point. The occurrence of the gel point has been identified with a rapid and sharp change in the relative rigidity of the system. The activation energy for the polymerization of a carboxyl-terminated polybutadiene with an aziridinyl compound has been measured as 13.8 kcal./mole.

The authors wish to thank Mr. Fred Davis and Mr. Cass Roquemore of the Techniques and Devices Group, Research Department, for their assistance in the construction of the instruments used in the experiments.

References

1. Lewis, A. F., and M. C. Tobin, *Trans. Soc. Rheol.*, **6**, 27 (1962).
2. Lewis, A. F., and J. K. Gillham, *J. Appl. Polymer Sci.*, **6**, 422 (1962).
3. Lewis, A. F., and J. K. Gillham, *J. Appl. Polymer Sci.*, **7**, 685 (1963).
4. Gillham, J. K., and A. F. Lewis, *J. Appl. Polymer Sci.*, **7**, 2293 (1963).
5. Gillham, J. K., and A. F. Lewis, *ACS Polymer Preprints*, **4**, 531 (1963).
6. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 351.

Résumé

L'expérience de Lewis et Gillham effectuée au moyen d'un pendule de torsion à tresse a été modifiée en vue d'obtenir les paramètres cinétiques des polymérisations effectuées avec des prépolymères visqueux. La courbe de rigidité relative a été interprétée en fonction de la durée de traitement. On a mesuré l'énergie d'activation de la polymérisation d'un polybutadiène a groupement carboxyle terminal avec un composé aziridinyle.

Zusammenfassung

Der Torsionsversuch mit Trägerfläche von Lewis und Gillham wurde derart modifiziert, dass kinetische Parameter bei der Polymerisation von hochviskosen Präpolymeren erhalten werden können. Die relative Steifigkeitskurve wird als Mass des Hartungsgrades benützt. Die Aktivierungsenergie der Polymerisation eines Polybutadiens mit Carboxylendgruppen mit einer Aziridinylverbindung wurde gemessen.

Received July 13, 1965

Revised August 31, 1965

Prod. No. 1288